

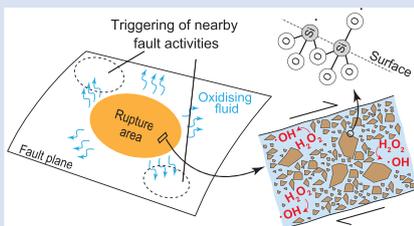
Generation of oxidising fluids by comminution of fault rocks

J. Kameda^{1*}, A. Okamoto²



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Abstract



Mechanochemical reactions exert a crucial control on the chemical environments of crustal fault zones during co-seismic and post-seismic periods. Comminution due to faulting causes activation of fault rock surfaces, such as the production of reactive radical species. In this study, we report on the generation of H_2O_2 by immersion of comminuted sedimentary, igneous, and metamorphic rocks that are broadly representative of those present at a variety of depths in subduction zones. Our experiments demonstrate that fresh surfaces of these rocks have an H_2O_2 productivity of 1.3–10.4 nmol m^{-2} (mean = 5.4 nmol m^{-2}). In a natural fault zone environment, H_2O_2 produced after a slip event is likely to react with Fe-bearing mineral surfaces or Fe^{2+} in

poorewater, or thermally decompose to produce more oxidative $\cdot\text{OH}$. The oxidising fluid produced by fault rupture in one patch may spread and induce corrosion and degradation of surrounding fault zones. These chemical processes are likely to be important factors influencing the interaction between neighbouring seismic activities.

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Introduction

Frictional slip on a fault zone causes comminution and wearing of fault rocks, producing highly reactive fine particles (Sammis *et al.*, 1986; Scholz, 2002). Radical species such as $\text{Si}\cdot$ and $\text{SiO}\cdot$ are commonly created on such particles of silicate minerals owing to homolytic rupture of Si-O covalent bonds (Hochstrasser and Antonini, 1972; Narayanasamy and Kubicki, 2005). Hydrogen (H_2) is a typical product that is generated by reaction between $\text{Si}\cdot$ and water molecules within a fault zone. The production of H_2 by the interaction of fluids and comminuted rocks has been demonstrated by laboratory experiments (Kita *et al.*, 1982; Kameda *et al.*, 2003; Hirose *et al.*, 2011) and that associated with seismic activity has been observed by field survey (Wakita *et al.*, 1980; Ito *et al.*, 1999). In addition, numerous studies have demonstrated that pulverisation of pure powders of minerals forming igneous rocks can produce oxidising compounds such as hydrogen peroxide (H_2O_2), superoxide ($\text{O}_2\cdot^-$), and hydroxy ($\cdot\text{OH}$) radicals (Schoonen *et al.*, 2006; Hurowitz *et al.*, 2007; Hendrix *et al.*, 2019), which are termed “reactive oxygen species” or “ROS”. ROS are formed by human activities such as mining, which produces fine particles of rocks and minerals (Schoonen *et al.*, 2006). ROS are also formed due to reaction with reactive secondary minerals and photochemistry in soils and sediments (*e.g.*, Georgiou *et al.*, 2015). Because fault activity causes comminution of fault rocks, it can be assumed that ROS are also produced within fault zones. Moreover, such ROS may modify the chemical and even physical state of the fault zone. For example, some lithologies such as shales have been shown to undergo a variety of degradation on interaction with H_2O_2 (formation of cracks and voids, decomposition and dissolution of constituent materials, *etc.*), which results in modification of their hydromechanical properties at varying

rates depending on temperature (Chen *et al.*, 2017; Zhou *et al.*, 2018; Yu *et al.*, 2019). Thus, the production and diffusion of oxidising compounds by a seismic event can potentially degrade surrounding fault zones and stimulate subsequent fault activity.

In this study, we examine the production of H_2O_2 by reaction between water and ground rock samples at ambient conditions. The samples are sedimentary, metamorphic, and igneous rocks that may constitute plate boundaries at various depths in subduction zones (Hacker *et al.*, 2003; Kimura *et al.*, 2012; Kameda *et al.*, 2017). Our results show that oxidising fluid can be easily produced throughout the plate boundary zone after an earthquake. On the basis of our findings, we discuss the importance of the chemical aspects of fluids on fault behaviours.

Samples and Experimental Methods

We analysed five natural rock samples: shale and oceanic basalt from the Cretaceous accretionary complex (Shimanto belt, Japan), and three basic schist samples from the high pressure Sanbagawa metamorphic belt, Japan. The basic schist samples (basic schist 1, basic schist 2, and basic schist 3) were taken from the chlorite, garnet, and albite–biotite zones of the Sanbagawa belt, respectively, which correspond to pressure–temperature (P - T) conditions ranging from greenschist to epidote–amphibolite facies (~ 300 to ~ 550 °C; Enami *et al.*, 1994). For comparison, quartz sand (Wako Purer Chemicals) was also used for the experiments.

Whole rock major element concentrations of the rock samples were determined by an X-ray fluorescence spectrometer (XRF; Rigaku 25X Primus IV) using the conventional glass bead method. The $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratios were determined by wet chemical

1. Department of Earth and Planetary Sciences, Faculty of Science, Hokkaido University, N10 W8, Sapporo, 060-0810, Japan

2. Graduate School of Environmental Studies, Tohoku University, Sendai, 980-8579, Japan

* Corresponding author (email: kameda@sci.hokudai.ac.jp)



analyses. Mineral compositions were analysed by X-ray diffraction analysis (XRD; MAC Science MX-Labo), and the obtained XRD patterns were used for quantitative analysis by RockJock software (Eberl, 2003).

The grinding experiments were carried out by using a planetary-type ball mill apparatus (P6; Fritsch). An amount of 3 g of each powder was loaded into a zirconia mill pot and was processed at 250–300 rpm for 5 min. The freshly ground powders with the post-grinding grain size of $\sim 0.5 \mu\text{m}$ (estimated from the surface area data described below, assuming uniform spherical particles) were then mixed with pure water (Direct-Q 3UV, Merck; pH = 5.84) in a Teflon beaker at room temperature ($\sim 22^\circ\text{C}$), and settled for 10–20 min. The H_2O_2 concentrations of the filtered solutions were then measured with the Scopoletin-Horseradish peroxidase (HRP) Fluorometric method using a fluorometer (RF-5300PC; Shimadzu). The post-experiment pH of the solutions was also measured. The specific surface areas of the processed powders were measured by the Brunauer-Emmett-Teller (BET) method using an automated sorption analyser (Autosorb, Quantachrome Instruments). More details on the samples and experimental methods are described in the [Supplementary Information](#).

Results

Our experiments demonstrated that all of the studied samples were able to produce H_2O_2 by mechanical activation and subsequent immersion in water. [Figure 1](#) shows the H_2O_2 productivity of each sample (nmol m^{-2}), which is calculated from the H_2O_2 concentration of the reacting fluid (the background H_2O_2 concentration of $0.060 \mu\text{mol L}^{-1}$ was subtracted from the measured concentration) normalised to the total surface area of the ground powders, as well as pH of the reacted solution and Fe^{2+} content in the solid samples ([Tables S-1, S-2](#)). The two analysed quartz samples have values of 0.55 and 0.44 nmol m^{-2} , which are slightly higher than previous results ($0.2\text{--}0.3 \text{ nmol m}^{-2}$; [Hurowitz et al., 2007](#)). Factors such as different temperatures, pH of the matrix, reaction time, hydration state of the samples, etc. could explain the differences. The H_2O_2 productivities of the natural rock samples are generally one order of magnitude greater than those of quartz, ranging from 1.3 nmol m^{-2} (shale) to 10.4 nmol m^{-2} (basic schist 3) with a mean value of $\sim 5.4 \text{ nmol m}^{-2}$.

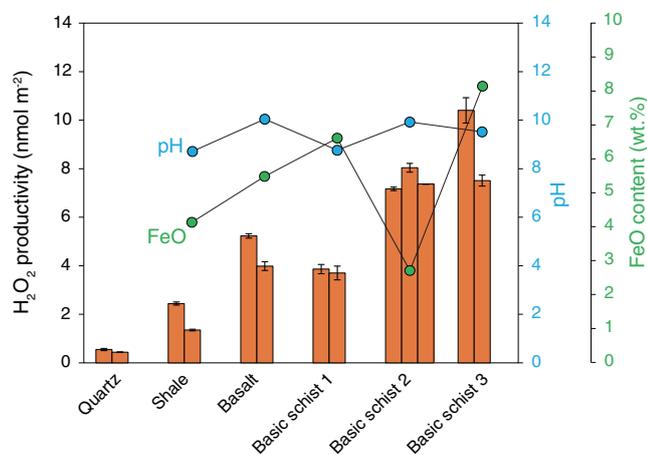
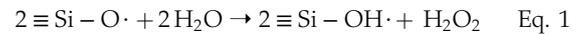


Figure 1 H_2O_2 productivity of the analysed samples. Error bars for H_2O_2 productivity were estimated from the equation for the standard addition method ([Larsen et al., 1973](#)). The pH of the solution after the experiment (during the duplicate analyses) and the concentration of FeO in the rock samples are also shown.

No obvious correlation was found between the H_2O_2 productivities and pH or Fe^{2+} content.

Discussion

Although the actual mechanism of H_2O_2 production from pulverised mineral surfaces is not completely understood, [Hendrix et al. \(2019\)](#) argued that $\text{Si-O}\cdot$ on a newly created mineral surface reacts with H_2O to generate H_2O_2 as follows:



[Hurowitz et al. \(2007\)](#) conducted pulverisation experiments using various pure mineral types and found that H_2O_2 productivity depends on the crystallographic nature of silicate minerals, with productivity increasing with a decreasing number of corners shared between Si (Al) tetrahedra (here termed the “ c ” number; [Fig. 2](#)). For example, tectosilicate minerals such as quartz and plagioclase have $c = 4$ and show the lowest H_2O_2 productivity of $< 1.0 \text{ nmol m}^{-2}$ of other types of silicate minerals with $c < 4$ ([Hurowitz et al., 2007; Fig. 2](#)). As the present work used rock samples that included different types of silicate minerals, the weighted mean of c of each sample was estimated by XRD analysis ([Table S-3](#)). [Figure 2](#) presents the relationship between H_2O_2 productivity and c of the analysed rock samples, and shows that the data are broadly consistent with the results of [Hurowitz et al. \(2007\)](#). Our results reveal that H_2O_2 can be generated by activation of natural rocks irrespective of their type (*i.e.* sedimentary, metamorphic, and igneous rocks), and the amount generated is likely to depend on the mineral composition of the rock.

Stability of H_2O_2 in fault zones following slip. Since fault movement causes comminution of fault rocks, H_2O_2 is expected to be produced by the reaction with porewater after an earthquake event. Furthermore, larger slip events may also lead to greater amount of comminution ([Scholz, 2002; Hirose et al., 2012](#)), which would produce more H_2O_2 . In a natural fault zone environment, generated H_2O_2 reacts with Fe-bearing mineral surfaces or Fe^{2+} in porewater to produce more oxidative $\cdot\text{OH}$, as follows (*i.e.* the Fenton reaction):

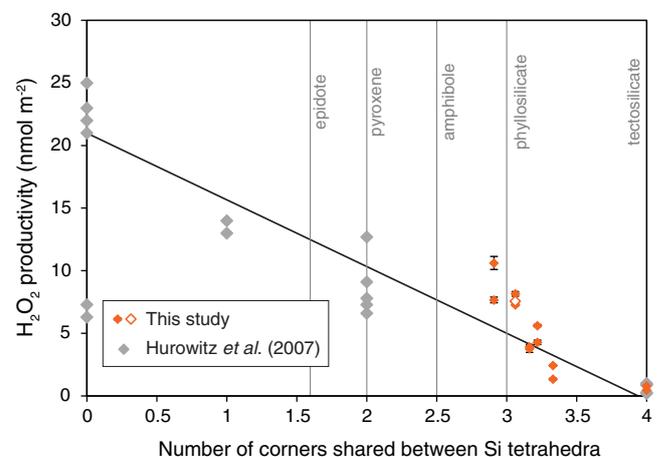
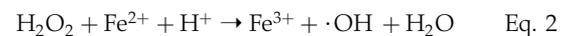


Figure 2 H_2O_2 productivity vs. number of corners shared between silica tetrahedra (weighted mean) for the analysed rocks. The open symbol is data for the experiment using 0.01 M NaCl solution. Data and regression line from [Hurowitz et al. \(2007\)](#) are also shown.

In addition, H_2O_2 decomposes to two $\cdot\text{OH}$ at high temperature conditions. The rate coefficient of the decomposition reaction is described as $k = 6.4 \times 10^5 \exp(-71 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$ (Takagi and Ishigure, 1985). This suggests that the half-life of H_2O_2 (i.e. $\ln(2)/k$) is 158 min at 100 °C but is only ~1 min at 200 °C. In the supercritical condition ($T > 374$ °C), the activation energy of the decomposition reaction can be higher (182 kJ mol⁻¹; Croiset *et al.*, 2004), but the half-life is again very short (e.g., several seconds at 400 °C). Thus, it is presumed that H_2O_2 quickly decomposes to $\cdot\text{OH}$ after an earthquake, and fluid containing these oxidative compounds may diffuse along the fault zone.

Influence of oxidising fluid generation on surrounding fault zones. In general, an earthquake does not occur in isolation but occurs as part of a sequence controlled by physical processes such as stress perturbation (Scholz, 2002). Porewater diffusion is usually invoked as a reason for aftershock sequence (e.g., Nur and Booker, 1972), but only the physical aspect of water (i.e. fluid pressure) has been argued in these models. Our study indicates the importance of chemical interaction between the fluid and surrounding fault zones. Specifically, generation of highly oxidising fluid can potentially promote corrosion of nearby fault zones and stimulate further fault activity. Such oxidising fluid is thought to interact with Fe-bearing minerals as well as organic compounds (Chen *et al.*, 2017; Zhou *et al.*, 2018). $\cdot\text{OH}$ oxidises even graphite (Wang and Zhang, 2018), a common product of the thermal maturation of organic compounds in metamorphic rocks, and may therefore degrade fault zones containing such minerals and materials. In natural examples, degradation or consumption of graphite has been observed in some fault zones (Nishiyama *et al.*, 1990; Kretz, 1996; Nakamura *et al.*, 2015), and the involvement of oxidising fluids in these processes has been suggested (Nishiyama, 1990; Okamoto *et al.*, 2021). In addition to mechanical processes, oxidative corrosion could promote such graphite degradation. However, it has not been fully clarified how the redox state of a fault temporally and spatially changes during the seismic cycle. For a more quantitative consideration, the kinetics of the reaction between oxidising fluid and various types of fault rocks and the lifetime of oxidising state of the fluid need to be clarified in future work, as well as how such fluid can affect the shear strength and frictional properties of the rock.

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Additional Information

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2131>.



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